



# Continuous elimination of gaseous dimethyl methylphosphonate by a photocatalytic flow reaction system



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## ABSTRACT

Dimethyl methylphosphonate (DMMP) removal by a continuous photocatalytic reaction system at different levels of humidity (RH) was investigated for the purpose of allowing rescue operations at disaster sites over an extended period of time when applied to gas masks or other protective gear. With a high flow rate of air (10 L/min), around 85% of the 0.17 μmol/L DMMP was successfully eliminated by this photocatalytic reaction system regardless of relative humidity. On the other hand, the formation of intermediates on the TiO<sub>2</sub> surface indicated that photocatalytic activity was dependent on relative humidity, and during a 5-h test period, the ratio of photocatalytic DMMP conversion reached 74.5% at 100% RH. DMMP adsorption onto the TiO<sub>2</sub> surface was found to be quite strong; DMMP removal was observed despite low humidity and dark conditions

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## 1. Introduction

Over the last decade, photocatalysis has been studied as one of the most progressive, green and low cost environmental remediation technologies which has been applied to such areas as the removal of automobile exhaust gas on highways and the development of self-cleaning materials. One of the applications for the elimination of gaseous pollutants is the photodecomposition of chemicals used in warfare. Various studies have been carried out on the elimination of gaseous dimethyl methylphosphonate (DMMP), a sarin simulant [1–11]. DMMP has a characteristic strong adsorption onto TiO<sub>2</sub> or other solid surfaces on which methanol is formed continuously by the hydrolysis of DMMP [2–6,8,9,12]. It is well known that, upon UV irradiation, DMMP on TiO<sub>2</sub> is photooxidized to CO, CO<sub>2</sub> and H<sub>2</sub>O – the major final products while methanol, formaldehyde, formic acid, methyl formate and dimethyl ether are formed as intermediates in the gas phase [1–6,8,9,11,13–15]. Moss et al. have reported that the adsorption and accumulation of nonvolatile phosphoric compounds, i.e., DMMP, methyl methylphosphonate (MMP), methylphosphonic acid (MPA) and phosphoric acid (PA) on the TiO<sub>2</sub> surface, cause great difficulty in

the removal of chemical agents used in warfare [6]. For its practical application, several investigations have been carried out on the effects of the relative humidity on the photocatalytic elimination of DMMP in batches. Trubitsyn and Vorontsov have examined the photocatalytic oxidation of low (0.9 μmol) and high (45 μmol) coverage of DMMP on TiO<sub>2</sub> at both 1% and 50% relative humidity (RH) [5]. They reported that, with high DMMP coverage quantity, the photocatalytic oxidation rate at 50% RH was slightly less than in the case of 1% RH. In contrast, Besov et al., who investigated the photocatalytic elimination of DMMP by TiO<sub>2</sub> aerosol at 4% and 37% RH, have reported that the rate of the photocatalytic oxidation was significantly increased with the rise in relative humidity [9]. Also, Kiselev et al. have examined the photocatalytic degradation of DMMP on rutile TiO<sub>2</sub> under dry and wet conditions (0% and 7% RH) [7]. They observed that the existence of a few water layers reduced the formation of intermediates on the TiO<sub>2</sub> surface and that the water layers preserved high photocatalytic activity. These results provide important information regarding the effects of relative humidity on gaseous DMMP removal in batches. Studies on DMMP removal under conditions of continuous flow have not yet been fully conducted, although necessary when considering actual situations in which the elimination of chemical warfare agents will be urgently required.

The final goal of our study is to develop a lightweight photocatalytic air-purifier combined with charcoal canister for gas masks

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designed to allow the extension of time for rescue operations. We have constructed a flow-type photocatalytic reaction system and have succeeded in carrying out the continuous removal of gaseous DMMP using a photocatalytic system. To simulate real-life situations, the concentration of DMMP-contaminated air was adjusted to the same level as that of sarin gas of LD<sub>50</sub>. The gas was then introduced into the reaction system at a flow rate of 10 L/min, which is higher than normal respiratory minute volume. We investigated DMMP elimination under various relative humidity conditions and identified the photooxidation products on the TiO<sub>2</sub> surface while continuously introducing DMMP-contaminated air into the reaction system.

## 2. Materials and methods

### 2.1. Preparation and characterization of the TiO<sub>2</sub>-coated silica foams

A commercial peroxy-modified anatase photocatalyst sol (SLEC-PA; Office Takahashi Inc., Saga, Japan) was used in this study [16,17]. SLEC-PA was immobilized onto doughnut-shaped silica foams (10 mm thick, 40 mm in diameter, 20 mm diameter hole, and 84% porosity; Fig. 1A) by a dip-coating method. Photocatalyst-immobilized silica foams were prepared as follows: sixteen pieces of the doughnut-shaped silica foams were dip-coated with SLEC-PA and were withdrawn at a speed of 1.5 mm/s. TiO<sub>2</sub>-coated silica foams were obtained after calcination at 450 °C for 1 h. These procedures (coating – calcination) were repeated three times. The total amount of TiO<sub>2</sub> on the 16 pieces of silica foam was 0.56 g, as calculated by subtracting the weight of the raw silica foams from the weight of the TiO<sub>2</sub>-coated silica foams. The TiO<sub>2</sub>-coated silica foam was characterized by the crystalline structure and SEM image. Rigaku SmartLab carried out observation of crystalline structure of the samples. The surface structure of TiO<sub>2</sub> coated silica foam was observed by Hitachi SEM-4700 field emission scanning electron microscope (FE-SEM). The specific surface area of photocatalyst is one of important factor for photocatalytic activity. However, observation of TiO<sub>2</sub> on the silica foam is difficult. Therefore, the specific surface area of the calcined SLEC-PA gel was measured by Quanta-chrome AS-1.

Fig. 1B shows the inside structure of the flow-type photoreactor and Fig. 1C shows a picture of the photoreactor. The photoreactor is cylindrical-shaped, 190 mm in length and 40 mm in internal diameter, and a quartz glass tube (19 mm in external diameter) was placed at the center of the reactor. Of the 0.185 L inside volume of the empty reactor, 0.15 L was available as an operational volume for the TiO<sub>2</sub>-coated silica foams (16 pieces). A UV lamp with a central wavelength of 352 nm (6 W Black light blue FL6BL-B; Hitachi Lighting Ltd., Tokyo, Japan) was placed inside the glass tube while the TiO<sub>2</sub>-coated silica foams were isolated from the UV lamp by the quartz glass tube. The TiO<sub>2</sub>-coated silica foams were pre-exposed to UV light for 1 h in order to remove the adhesive organic compounds from the TiO<sub>2</sub> surface. The UV light intensity at the surface of the TiO<sub>2</sub>-coated silica foams in this system was measured at 7.2 mW/cm<sup>2</sup>, using a UD-36 UV Radiometer (Topcon Co., Tokyo, Japan). Dimethyl methylphosphonate (DMMP, Tokyo Chemical Industry Co., Tokyo, Japan) was used as the sarin simulant.

### 2.2. Flow-type photoreactor, continuous photocatalytic reactions, gas and ion chromatographs

The flow-type photocatalytic reaction system is shown in Fig. 2. Air was used as the carrier gas and was dried by passing through a membrane dryer (DM-XB05; Ube Industries, Ltd., Tokyo, Japan) and silica gel. The dried air was separated into the three ways: to

the water bubbler (generation of wet air), DMMP bubbler (generation of gaseous DMMP), and to the mass-flow controller for dry air. DMMP mist generated by bubbling was removed in a mist trap before being mixed with dry air. The concentration of DMMP was controlled at 0.17 μmol/L in the carrier gas. The flow rate of the DMMP-mixed air was adjusted to 10 L/min, which is larger than the respiratory minute volume in normal conditions. The concentration of DMMP was determined to be 0.17 μmol/L (=1.7 μmol/10 L) as it was about the same level as a 50% lethal dose, or LD<sub>50</sub>, of sarin gas (around 20 ppm). The relative humidity (RH) of the DMMP-mixed air was adjusted to 0%, 50% and 100% by controlling the flow rates of dry and wet air. All of the experiments were carried out at a room temperature of around 25 °C.

A gas chromatograph GC-2014 (GC; Shimadzu Co., Kyoto, Japan) was used to analyze the gas components every 12 min. The outlet gas was automatically injected into the GC through a stainless steel tube that was connected directly to the photocatalytic system. A Rtx-1 capillary column (30 m length × 0.53 mm diameter × 5.0 μm thickness, Shimadzu GLC, Ltd., Kyoto, Japan) was used for temperature-programmed analysis by GC (from 50 °C to 80 °C). The organic compounds (intermediates of DMMP) and phosphoric compounds (DMMP and its intermediates) in the gas phase were detected by FID and FPD, respectively. First, the path of the gas flow was switched from bypass to the photoreactor after confirming the initial concentration of the DMMP gas. The residence time of the gas in the photoreactor was around 0.9 s (as 10 L/min). The path of the gas flow was switched back to bypass after the reaction. After the experiment, the TiO<sub>2</sub>-coated silica foams (16 pieces) were removed from the photoreactor, dipped in 400 mL ultra pure water for 30 min, and the washings were analyzed by an ion chromatograph IC-2001 (IC; Tosoh Co., Tokyo, Japan). The concentrations of the intermediates – methylphosphonic acid (MPA) and phosphoric acid (PA) – and the final products were then analyzed by IC.

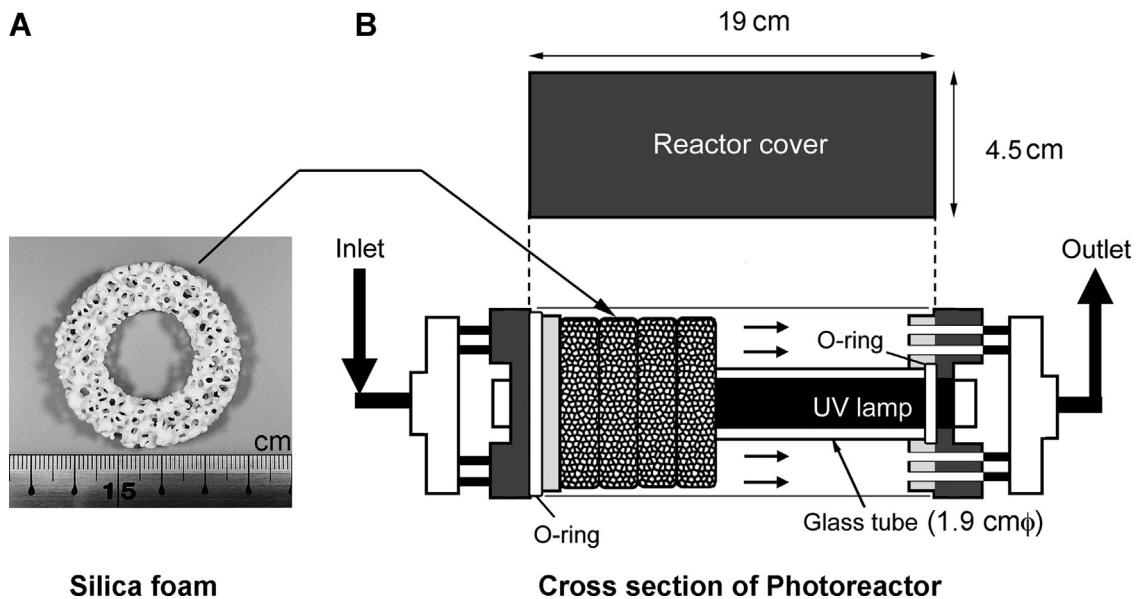
## 3. Results and discussion

### 3.1. Characteristics of photocatalyst

The photocatalyst, SLEC-PA which we used, is a commercialized material. However, this photocatalyst is not yet widely known in the world. We will show the details of the characteristics of this photocatalyst. Fig. 3 shows the surface structure of TiO<sub>2</sub>-coated silica foam. As shown in the Fig. 3A, TiO<sub>2</sub> was partially peeled off from the substrate. SiO<sub>2</sub> foam itself is relatively fragile and we predicted that the peeled off was partially occurred. By the high-resolution observation of the TiO<sub>2</sub> silica foam, it is clarified that TiO<sub>2</sub> layer had many nanopores as shown in Fig. 3B. It is expected that the specific surface area of TiO<sub>2</sub> must be large. Consequently, the specific surface area of calcined SLEC-PA was observed, and the result was 99.84 m<sup>2</sup>/g. This value is twice of P25 (Evonik), and it is considered that the surface area of TiO<sub>2</sub> coated silica foam was enough for photocatalysis. Fig. 4 shows the XRD observation results. As shown in Fig. 4A, silica foam had a quartz structure [18], on the other hand, these quartz structure was hidden by TiO<sub>2</sub> coating as shown in Fig. 4B. The crystalline structure of TiO<sub>2</sub> on the silica foam was mainly anatase phase, however, one sharp peak was found at around 30. It is expected that this 2θ value be attributed to TiO<sub>2</sub> brookite phase [19].

### 3.2. Removal of DMMP by continuous photocatalytic reactions

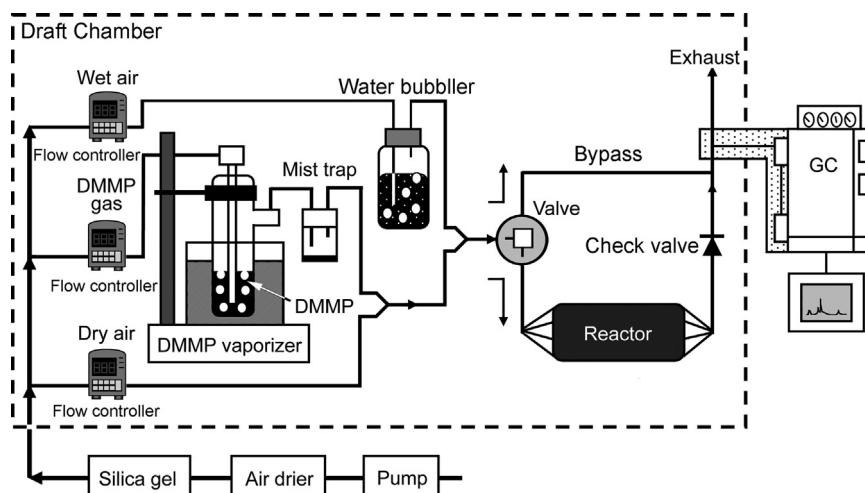
For practical applications in such protective equipment as gas masks, guarantees of long life and safety are required for the products as well as allowance for relative humidity. We have, thus, investigated the effect of the relative humidity on the



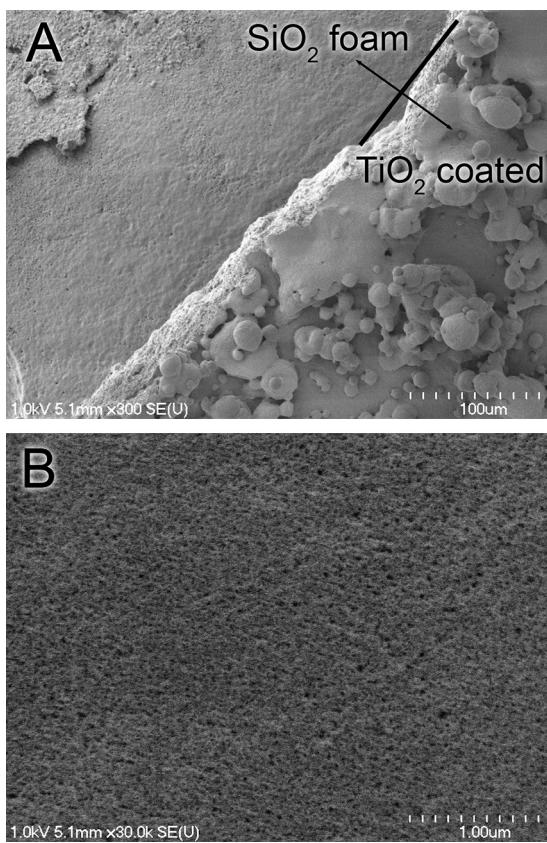
**Fig. 1.** Design of the photoreactor. (A) Shape of the silica foam.  $\text{TiO}_2$  was coated onto this foam. (B) Cross section of the photoreactor.

continuous photocatalytic degradation of DMMP. The time courses of the changes in DMMP concentrations upon UV irradiation are shown in Fig. 5A and the time courses of the changes in DMMP concentrations under dark conditions are shown in Fig. 5B. In these experiments, DMMP gas was introduced into the photoreactor and UV irradiation was started after confirmation of the initial DMMP concentration for 30 min flow. However, this 30 min gas flow might be short in these experiments because the gas concentration of DMMP after turning off the UV light was higher than before turning on the UV light. The best method to take a balance of DMMP concentration between start and end is the taking of enough time (at around 8 h) for stable of DMMP concentration at the initial condition before UV irradiation. It is predicted that the difference of concentration between the initial and the end of UV irradiation is derived to adsorb of DMMP gas to the inside of pipeline. However, we could not wait until stability of DMMP gas concentration, therefore the initial concentration of DMMP gas was generally lower than the end of experiment. As shown in Fig. 5A, DMMP itself was not observed at the outlet of the photoreactor until 1 h had passed and thereafter, the concentration of DMMP gradually increased. In this experiment, no meaningful differences in DMMP elimination

were observed with the difference in the relative humidity experiment, and the DMMP removal ratio reached as high as around 85% during 5 hour UV irradiation. To confirm whether it was caused by DMMP photolysis, we carried out the same experiment without the  $\text{TiO}_2$ -coated silica foams. In this experiment, the relative humidity was fixed at 50% RH because no significant influence of the relative humidity on DMMP elimination was observed, as mentioned above. The concentration of DMMP was not changed by UV irradiation, as shown in Fig. 5A. These results show that gaseous DMMP was not decomposed by photolysis with UV irradiation alone at a flow rate of 10 L/min. Here, we also confirmed the thermal efficiency for DMMP degradation. Thermo-couple was inserted to the photocatalytic reactor, and we observed the changes of temperature after turn on the UV light with 10 L air flowing. As a result, the temperature increasing was stabled at around 30 °C since the large flow rate of air was effectively cooled down of the reactor. Under the high rate mass-flow condition (contact time is 0.9 s), we do not need to think the hydrolysis of DMMP by the thermal effect. From the result of Mitchell et al., DMMP did not react on the  $\text{Fe}_2\text{O}_3$  at 30 °C for 1 h. DMMP did not also react at 50 °C at the surface of the other metal oxides, such as  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  and  $\text{La}_2\text{O}_3$  [20].



**Fig. 2.** Scheme of the experimental setup.



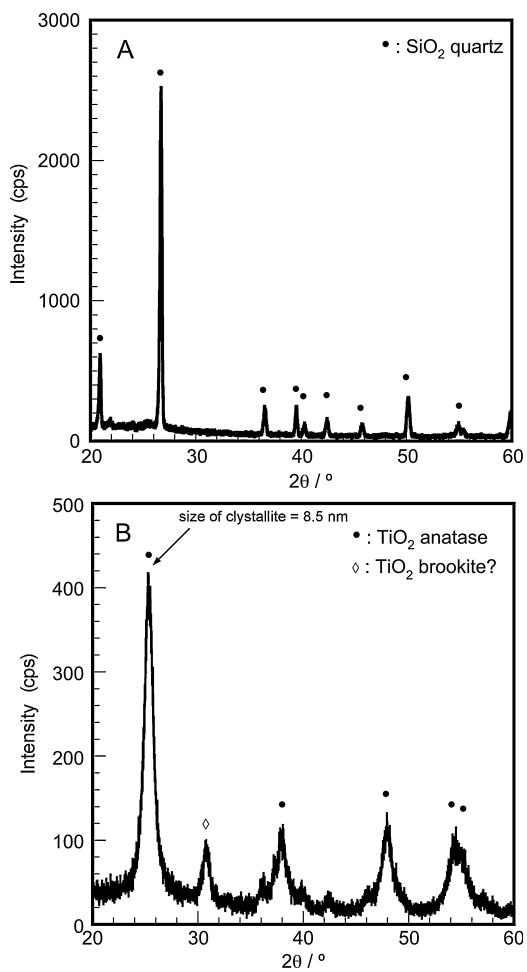
**Fig. 3.** SEM image of the  $\text{TiO}_2$  coated silica foam. (A) Low resolution and (B) high resolution.

Therefore, we concluded that the factor of temperature in the reactor for DMMP degradation is negligible.

Elimination of DMMP caused by adsorption and hydrolysis on  $\text{TiO}_2$ -coated silica foams under the dark condition is shown in Fig. 5B. The concentration of DMMP after introduction into the photoreactor decreased immediately, and the removal ratio of DMMP reached 100%. However, the time elapsed before DMMP recovered to its initial concentration was dependent on the relative humidity, i.e., after 5 h, 3 h, 2 h at 0%, 50%, 100% RH, respectively. Comparison of the results of the experiments with and without UV irradiation indicated that these decreases in DMMP concentrations were attributed both to adsorption and photocatalysis. The gaseous intermediates of DMMP were detected methanol alone under high relative humidity conditions by photocatalysis and/or hydrolysis. Other products such as formaldehyde, formic acid and dimethyl ether that were generated in batch condition [1–6,8,9,11,13–15] were either not identified or smaller in amount than the observation limit of GC. In these experiments, the concentration of DMMP after the end of experiment was higher than that of the start of experiment. The reason of this result is depend on the shift of the GC baseline with progress of the time. This shift was also observed on the bypass position (Fig. 2).

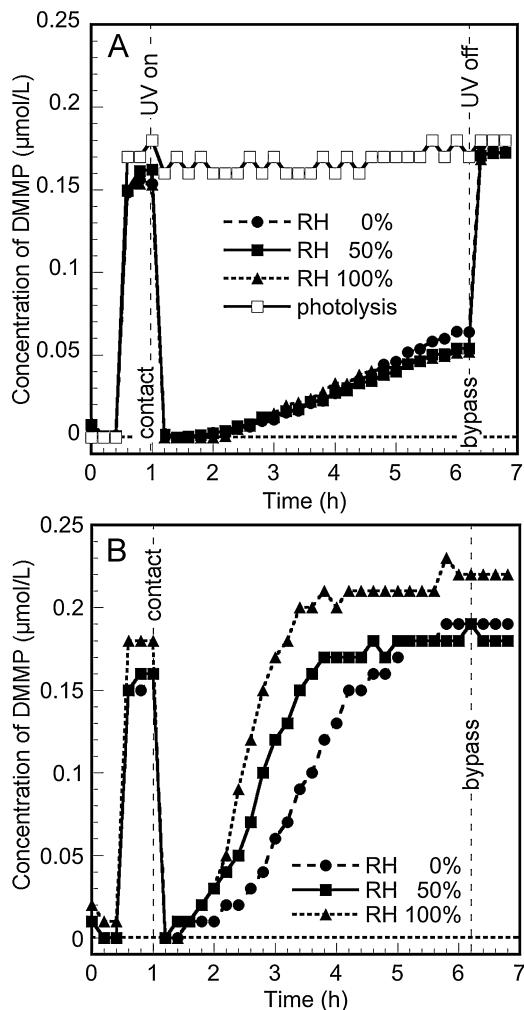
Fig. 6 shows the time courses of methanol formation in the gas phase by photocatalysis (Fig. 6A) and under dark conditions (Fig. 6B). In this study, although methanol concentrations were relatively low and insufficient in quantity for analysis, changes in the amount of methanol formation with different relative humidity conditions were observed. As shown in Fig. 6A, methanol formation with photolysis of DMMP was not observed under 50% RH, and these results are in good agreement with Fig. 5A.

From these experimental results, it was clarified that the changes in relative humidity influence methanol formation



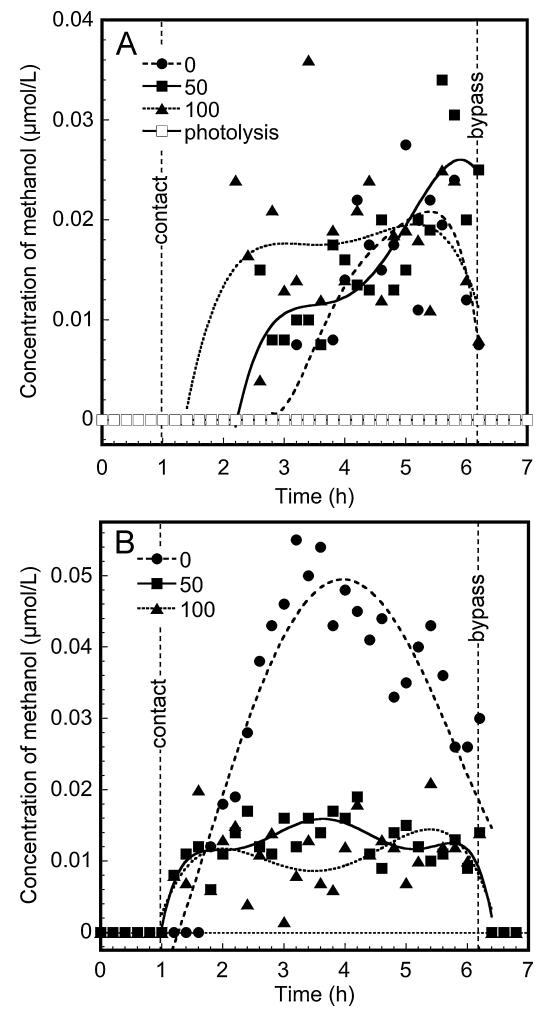
**Fig. 4.** XRD pattern of  $\text{TiO}_2$  coated silica foam. (A) Silica foam and (B)  $\text{TiO}_2$  coated silica foam.

behavior in the gas phase, i.e., methanol formation caused by the degradation of DMMP was observed after 2 h, 1.5 h and 1 h at 0%, 50% and 100% RH, respectively. In addition, methanol concentrations in the gas phase increased with the progress of photocatalysis. Fig. 6B shows the time courses of the methanol concentrations in the gas phase under dark conditions. Methanol concentrations at 0% RH did not correlate with the other conditions, it is considered that faults in the experimental operations under 0% RH may be responsible for these results. The formation of methanol was immediately observed after contact of DMMP to the photocatalyst under dark conditions regardless of the relative humidity. The concentrations of methanol remained constant while DMMP was flowing into the photoreactor. It is expected that methanol formation from DMMP under dark condition was caused by the contact catalysis on the  $\text{TiO}_2$  surface. Trubitsyn and Vorontsov have reported that the hydrolysis of adsorbed DMMP on  $\text{TiO}_2$  led to methanol formation [5]. Sheinker and Mitchell have reported that methanol as a volatile product was observed on  $\gamma$ -alumina at room temperature [14]. Our experimental results were consistent with these previous results. Generally, a solid surface is required for the hydrolysis of DMMP to occur.  $\text{TiO}_2$ -coated silica foams have a large surface area and it is considered that despite the high flow rate (10 L/min), DMMP still comes into contact with  $\text{TiO}_2$  a multitude of times (the residence time of gaseous DMMP in the photoreactor was around 0.9 s, as shown in the Experimental section). Trubitsyn et al. mentioned that the quantity of DMMP was too large for complete hydrolysis over the given quantity of  $\text{TiO}_2$  [5]. In our case, the  $\text{TiO}_2$  surface after 6 hour DMMP gas flow was wet under dark condition, and



**Fig. 5.** Changes in the gaseous DMMP concentration upon UV irradiation (A) and in dark conditions (B) under various relative humidity.

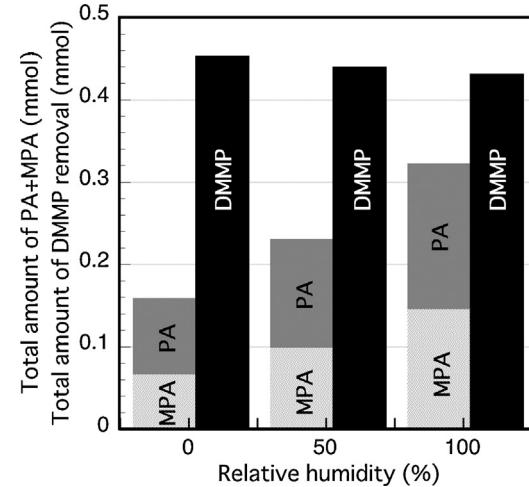
there is no longer any doubt about excess adsorption of DMMP on TiO<sub>2</sub> surface. During photocatalysis, the time lag for the detection of methanol in the gas phase was observed with a difference in the relative humidity. It is considered that methanol itself was formed with photocatalysis and hydrolysis of DMMP. The formed methanol was also photodecomposed by TiO<sub>2</sub> [10], and thus, methanol formation was not observed at the early stage of the photocatalytic reaction. However, the number of active sites on the TiO<sub>2</sub> surface decreased with the progress of photocatalysis and hydrolysis by the adsorbed H<sub>2</sub>O, DMMP, and its intermediates. The discussion of active sites is speculation. However, from the result of Trubitsyn et al. [5] and Sato et al. [21] excess adsorption of Salin and DMMP derived from excess injection of them formed the multi layer on TiO<sub>2</sub> surface, and it is expected that the formation of this multi layer bring the decrease of active sites on TiO<sub>2</sub>. As a result, although delayed, methanol formation in the gas phase was observed. The higher the relative humidity, the sooner the formation of methanol appeared. These results show that the TiO<sub>2</sub> surface was covered by H<sub>2</sub>O derived from water in air at the early stage of the reaction while water layers on the TiO<sub>2</sub> surface inhibited the re-oxidation of the formed methanol. Methanol concentration after the photodegradation of DMMP was around 10 times lower than that of the introduced DMMP. We expect that this level of gaseous methanol can be easily removed by the absorbency of gas mask charcoal canister when the photocatalytic reactor is combining to the gas mask.



**Fig. 6.** Changes in the gaseous methanol derived from DMMP upon UV irradiation (A) and in dark conditions (B) under various relative humidity.

### 3.3. DMMP decomposition products by continuous photocatalysis

In order to confirm the products for continuous DMMP photodegradation, the adsorbed compounds on the TiO<sub>2</sub> surface were analyzed by IC. Fig. 7 shows the total amounts of removed DMMP



**Fig. 7.** Total amount of DMMP removal and formed PA + MPA under UV irradiation (with photocatalysis), in different relative humidity.

**Table 1**

Summary of DMMP removal by the difference of UV irradiation and dark condition.

| Condition | Relative humidity (%) | Total amount of DMMP introduction (mmol) | Total amount of DMMP removal (mmol) | Ratio of DMMP removal (%) | Formed PA (mmol) | Formed MPA (mmol) | Amount of byproducts + final products (mmol) | Formed MeOH (mmol) | Ratio of DMMP transition (%) | Amount of remained DMMP on TiO <sub>2</sub> (mmol) |
|-----------|-----------------------|--|-------------------------------------|---------------------------|------------------|-------------------|--|--------------------|------------------------------|--|
| UV on     | 0                     | 0.531                                    | 0.453                               | 85.2                      | 0.093            | 0.066             | 0.159  | 0.029              | 35.1                         | 0.078  |
|           | 50                    | 0.513                                    | 0.441                               | 86.0                      | 0.132            | 0.099             | 0.231  | 0.034              | 52.4                         | 0.072  |
|           | 100                   | 0.507                                    | 0.432                               | 85.1                      | 0.177            | 0.145             | 0.322  | 0.045              | 74.5                         | 0.075  |
|           | 0                     | 0.570                                    | 0.281                               | 49.4                      | 0.000            | 0.000             | 0  | (0.101)            | 0                            | 0.289  |
|           | 50                    | 0.540                                    | 0.181                               | 33.6                      | 0.002            | 0.000             | 0.002  | 0.038              | 1.2                          | 0.359  |
|           | 100                   | 0.630                                    | 0.181                               | 28.8                      | 0.012            | 0.001             | 0.013  | 0.033              | 7.2                          | 0.449  |

and adsorbed organic/inorganic phosphoric acids on the TiO<sub>2</sub> surface under continuous photocatalytic reaction for 5 h. After photocatalysis, phosphoric acid (PA) and methylphosphonic acid (MPA) were observed as the main adsorbed components on the TiO<sub>2</sub> surface [1,13]. Trace amounts of methyl methylphosphonate (MMP) were also detected. Analysis of MMP was impossible, however, because the amount of formed MMP was extremely small and the range of retention time in IC between MPA and MMP was too close. Moreover, general organic acids such as formic acid and acetic acid were not detected in this analysis. This result is slightly different from the photodegradation of DMMP in aqueous phase. In this result, total amount of MPA + PA was lower than the amount of DMMP introduction. However, we mentioned that any intermediates and final products except for MMP, MPA and PA were not observed. Therefore, the difference of total amount of formed MPA and PA from DMMP introduction may be remained on the surface of TiO<sub>2</sub>. This expected amount of remained DMMP on TiO<sub>2</sub> surface (= [amount of introduced DMMP] – [amount removed DMMP]) was shown in Table 1. The surface of TiO<sub>2</sub> coated silica foam after photocatalysis was moisturized by anything under any humidity condition. The liquid layer may be mixture of MPA + PA, adsorbed DMMP and water. In this experiment, we observed MPA and PA by washings of TiO<sub>2</sub> coated silica foam after photocatalysis. It is considered that the difference of the amount of DMMP removal and the amount of MPA + PA as shown in Fig. 7 may be equal to the adsorbed DMMP on TiO<sub>2</sub> surface without reaction. In our previous study, we found the formation of formic acid, on the other hand, formation of MPA and MMP was not observed with photocatalysis of DMMP in aqueous phase at  $1 \times 10^{-4}$  m/L. We explained the reason of MPA undetected in an aqueous phase with TiO<sub>2</sub> photocatalyst in our paper [22]. On the contrary, continuous DMMP feeding system in this paper, it is easily understand that the increase of intermediates and final product with photocatalysis. Now on time, we do not have reasonable reason why formic acid was not observed, and additional research will be required.

While the total amount of removed DMMP was almost constant under the various relative humidity conditions as shown in Table 1, and the total amounts of PA and MPA increased with an increase in the relative humidity, as shown in Fig. 7. The total amount of PA + MPA within photocatalytic reaction was increased with increase of relative humidity ( $0.093 + 0.066 = 0.159$  mmol/5 h for 0% RH,  $0.132 + 0.099 = 0.231$  mmol/5 h for 50% RH and  $0.177 + 0.145 = 0.322$  mmol/5 h for 100% RH), and this total value becomes close to the total amount of DMMP removal. We did not observe the amount of remained DMMP on the surface, however, it is expected that the difference between amount of PA + MPA and DMMP removal is almost equal to DMMP remained onto the surface of TiO<sub>2</sub> coated silica foam. At least, 74.5% of DMMP under 100% RH was degraded under continuous photocatalytic reaction as shown in Fig. 5B, and this value is vastly different from the adsorption without photocatalysis. Table 1 shows the value obtained for the following: total amount of introduced DMMP both with/without UV irradiation, total amount of DMMP removal, rate

of DMMP removal, total amount of phosphoric acid, methylphosphonic acid, methanol, the final products and intermediates, and the decomposition rates from DMMP to the final products and intermediates, for 5 h at 0%, 50% and 100% RH. Under dark conditions, the total amount of the final products and intermediates generated by DMMP removal was only 7.2% at 100% RH. It is known, however, that DMMP cannot be oxidized to CO<sub>2</sub> by hydrolysis alone [14]. The total amount of adsorbed DMMP on the TiO<sub>2</sub> surface was, thus, calculated by subtracting the amount of DMMP removal from the total amounts of PA and MPA, as shown in Fig. 8.

Methanol, formaldehyde, formic acid, dimethyl ether and methyl formate are known to be the primary intermediates generated by DMMP photooxidation [1–6,8,9,11,13–15]. However, under the present flow system, since the absolute surface area of TiO<sub>2</sub> is relatively large for the total amount of the introduced DMMP, the intermediates formed were re-oxidized by photocatalysis on TiO<sub>2</sub> or in the liquid layer of DMMP and/or MPA + PA-dissolved DMMP liquid layer on TiO<sub>2</sub>. These intermediates were finally mineralized by photocatalysis. The expected photodecomposition route of DMMP is shown in Fig. 9. Some previous papers have reported that the strong adsorption and accumulation of phosphorus compounds (MMP, MPA and PA) as the principal products on TiO<sub>2</sub> causes the deactivation of photocatalysis [1,2,5–7,9,11]. However, the effect of deactivation of the photocatalyst by accumulated intermediates was considered to be insignificant in this 5-hour experiment. We observed methanol and MPA as intermediates of DMMP photocatalysis. Moss et al., reported that DMMP decomposed to H<sub>3</sub>PO<sub>4</sub> via MPA by photocatalysis [6]. Methanol is formed at the each step of photodegradation of DMMP and its intermediates. This methanol is photodecomposed to CO<sub>2</sub> and H<sub>2</sub>O via formic acid. We also found that the formation of MPA by photocatalysis, and it is expected

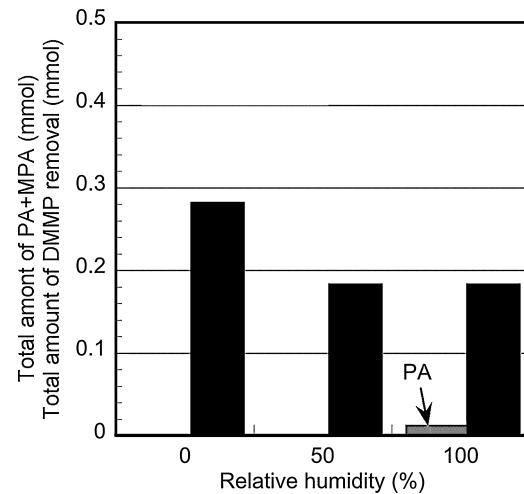
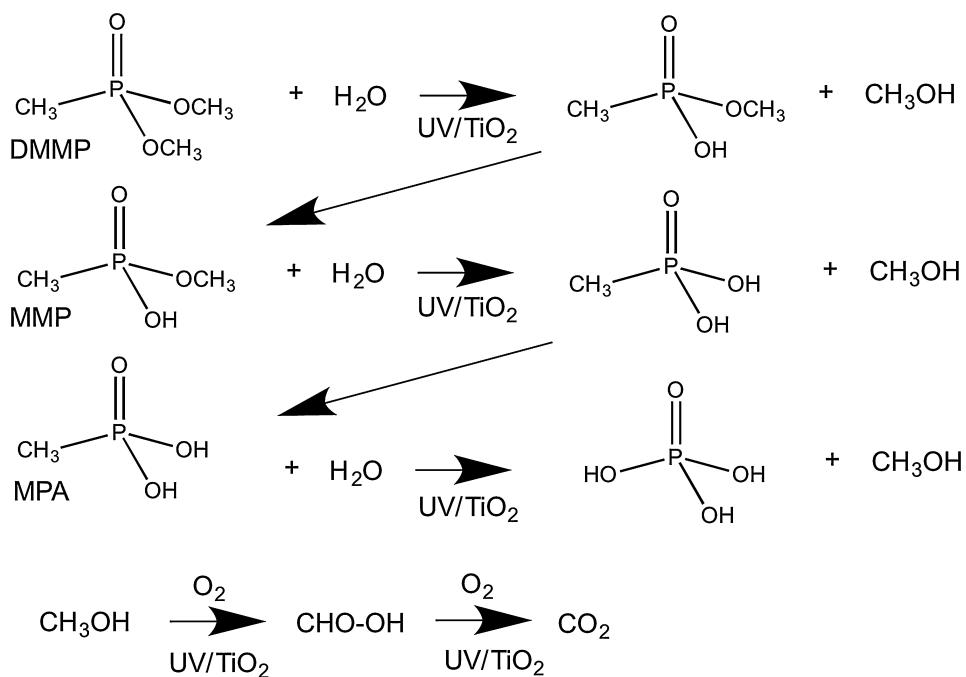


Fig. 8. Total amount of DMMP removal and formed PA + MPA under dark conditions (hydrolysis alone), in different relative humidity.



**Fig. 9.** Expected photodecomposition route of DMMP.

that the methoxy group in DMMP was oxidized by photocatalysis. Comparison of their results and our results, our expected photodegradation scheme of DMMP is shown in Fig. 9. Here, Moss et al. reported that the formation ratio of formic acid is quite low compare with the methanol formation [6]. In our experiment, we could not detect formic acid from the washings of TiO<sub>2</sub> coated silica foam after photocatalysis. We expected that the formation of formic acid was very small, as a result, we could not find the formation of formic acid.

This study can be expected to contribute to the development of innovative and effective protective gear and equipment that takes full advantage of the detoxification functions of photocatalysts for situations in which the air is contaminated with chemical warfare agents such as sarin gas. Zuo et al. have reported on the photolysis and photocatalysis of five chemical warfare agent vapors, sarin (GB), soman (GD), sulfur mustard (HD), cyanogen chloride (CK) and perfluoroisobutylene (PFIB), in batches. They have reported that GB, GD, HD might possibly undergo a photo-induced polymerization under UV light irradiation and that only CO<sub>2</sub> in the gas phase was detected during the photocatalysis of GB, GD, HD and PFIB [23]. They concluded that a dynamic photocatalysis approach was considered feasible for decontamination of air polluted by GB vapor. Hirakawa et al. have reported the adsorption and photocatalytic degradation of GB on TiO<sub>2</sub>, in which they showed that innocuous isopropyl methylphosphonic acid (IMPA) was formed with GB adsorption onto the TiO<sub>2</sub> surface by hydrolysis, and consequently, the adsorbed GB and IMPA on TiO<sub>2</sub> were quickly decomposed by photocatalysis [24]. In this study, a slight amount of methanol in the gas phase was generated from gaseous DMMP by photocatalysis. However, gaseous 2-propanol generated from GB by photocatalysis is less harmful than methanol so that activated carbon or other adsorbent columns may quickly remove this intermediate.

These results indicate that such a photocatalytic system, when combined with equipment such as gas masks currently available, would enable the extension of rescue operations; thus there are many possibilities for the development of innovative protective gear and equipment to be used at disaster sites. It should be noted that this continuous photocatalytic reaction system was not affected by the changes in the relative humidity. In addition, this

system has strong adsorption efficiency even without photoirradiation due to the wide surface area of TiO<sub>2</sub> for the amount of DMMP. These characteristics would, thus, enable the use of such equipment in sudden, unexpected situations such as a power breakdown, although photocatalysis is essential for maximum performance of the “photoreactor-combined” protective equipment.

#### 4. Conclusion

The continuous photocatalytic removal of 0.17 μmol/L DMMP at a flow rate of 10 L/min was successfully carried out. A high ratio for DMMP elimination of around 85% for up to 5 h was retained regardless of the differences in relative humidity. A high ratio for DMMP elimination by photocatalysis of around 85% for up to 5 h was retained regardless of the differences in relative humidity. The high performance of this system was due to the combined effects of adsorption, catalysis and photocatalysis. However, the highest contribution for removal of DMMP was the photocatalysis under UV irradiation, and this was confirmed by the comparison of the experimental results under dark conditions. The only harmful intermediate emitted to the gas phase throughout this experiment was methanol, although the concentration was low. The photocatalytic activity and adsorption efficiency of the photocatalyst for the elimination of DMMP were observed to decrease with the reaction time. This is explained by the accumulation of such byproducts as methylphosphonic acid and phosphoric acid. However, for the 5 h period of the photocatalytic reaction, the accumulation of such byproducts did not inhibit DMMP elimination in this reaction system. From these experimental results, we are expecting that combining of our photocatalytic reaction system and the charcoal canister of any protective gear and equipment currently in use can achieve significant time extension for rescue operations at disaster sites.

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